

## OXIDATION KINETICS OF COATED SILICON CARBIDE FIBER-REINFORCED SILICON CARBIDE (SiC/SiC)

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Silicon carbide fiber-reinforced silicon carbide (SiC/SiC) was exposed for 100 hours to dry, flowing oxygen. Oxidation kinetics were determined via thermogravimetric analysis at 981°, 1204° and 1316°C (1800°, 2200° and 2400°F). The effectiveness of three external coating systems applied for oxidation protection is discussed. In all cases, weight gains were observed, and the pyrolytic carbon interface layer remained intact. A CVD SiC external coating is the most promising due to low oxidation kinetics resulting from solid silica formation. A borosilicate glass was observed on the surface of two of the materials that have boron-containing coatings.

## Introduction

The low density and high temperature capability of continuous fiber-reinforced ceramic matrix composites (CMCs) makes this class of materials appealing for advanced aerospace engine applications. Continuous fiber reinforcement of Si-based matrices allows graceful failure if a component is damaged. An interface material is needed to prevent fiber/matrix bonding during fabrication. This material must also debond under high applied stress to dissipate matrix crack energy. In many composite systems, carbon is the interface material of choice. The major drawback of carbon is that it oxidizes at temperatures much lower than the intended use temperatures of CMCs. An extensive literature review of carbon oxidation in CMCs is beyond the scope of this paper. References 1-3 provide analysis of the oxidation of carbon in SiC/SiC systems, as well as appropriate literature reviews.

One approach used to protect the exposed carbon interface in these materials is

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to apply an oxidation-resistant external coating. One such coating is SiC deposited via chemical vapor deposition (CVD). If crack-free, this coating would provide satisfactory protection of the carbon. Oxidation would be further impeded by the solid silica layer formed on SiC at high temperature. However, if cracks do occur in this coating, oxidation will proceed at a rapid rate nearly independent of the crack opening displacement.<sup>3</sup> An alternative coating system comes directly from technology used to protect carbon/carbon (C/C). A SiC coating applied to C/C will be cracked due to thermal expansion mismatch. A glass-forming particulate such as boron can be added to the matrix<sup>4</sup>, or a glass-forming sealant layer can be applied to the C/C.<sup>5</sup> If the outer CVD SiC becomes cracked, the particulate or sealant can react with oxygen to produce a glass that seals the crack and inhibits oxidation. This technology is currently being applied to SiC/SiC composites.

Reliable CMCs are now being developed that possess good mechanical properties and oxidation resistance. The response of CMCs to high temperature environments can therefore be determined. The purpose of this paper is to expose one such silicon carbide fiber-reinforced silicon carbide (SiC/SiC) to a dry, flowing oxygen environment. The oxidation kinetics are determined via thermogravimetric analysis. The effectiveness of three different external coating systems in protecting the carbon interface is presented.

#### Experimental Procedure

The material used in this study (BFGoodrich Aerospace) is based on a 2D plain-weave 0/90° Nicalon™ (Nippon Carbon Co., Tokyo, Japan) fiber fabric layup. Material properties are listed in Table I. The fiber/matrix interface material is pyrolytic carbon 0.3 microns thick. The 114 × 254 mm preform is densified with silicon carbide via chemical vapor infiltration (CVI). Specimens were machined from the large panel into their final geometry of 25.4 × 13.0 × 3.5 mm. Because these samples were machined after densification was completed, the fiber edges and carbon interface were not sealed by SiC. These uncoated samples will be referred to as Type U. Three different coating systems were

**Table I. Material Description & Properties**

Fiber Content	45 volume %
Density	2.54 g/cc
Porosity	10 volume %
Tensile Strength	215 MPa
Tensile Modulus	183 GPa
CTE	$3.0 \times 10^{-6}/^{\circ}\text{C}$

applied on additional SiC/SiC samples: Type A, a SiC via chemical vapor deposition; Type B, a particulate-based sealant with an outer layer of CVD SiC; and Type C, a boron-rich inner layer with an outer layer of CVD SiC. Polished cross sections (to 20 microns) show details of the three different types of coatings (Figure 1). During the CVI technique, infiltration of the fiber weave becomes more difficult with time as porosity decreases. This often results in the formation of a layer of SiC on the surface of the composite. This layer can be seen in the upper portion of the Fig. 1 photos between the respective coatings and the SiC/SiC substrate. Cracks were observed in this layer in the as-received material in all three cases.

Oxidation experiments were conducted in dry oxygen flowing at 100 cm<sup>3</sup>/min in a vertical alumina tube furnace. Three temperatures were investigated: 981°, 1204° and 1316°C (1800°, 2200° and 2400°F). One must be aware that Nicalon fibers contain excess carbon and SiO<sub>2</sub>. At temperatures above 1200°C, Nicalon decomposes to form CO.<sup>6,7</sup> The oxidation kinetics were obtained by thermogravimetric analyses. Weight change was continuously monitored with a recording microbalance (C-1000, Cahn Instruments, Inc., Cerritos, CA). Samples were held in an alumina cup with an inner sleeve of fused silica. Exposure time was 100 hours.

Sample morphologies were studied via scanning electron microscopy (SEM, JEOL JSM-840A, Tokyo, Japan). The microscope was equipped with thin-window, energy dispersive spectrometry (EDS, KEVEX 3600-0178, Foster City, CA) that allowed elemental dot mapping of polished cross sections. Polished cross sections were prepared by sawing each sample in two, and polishing to a 20 micron finish with high-purity kerosene. Samples were then cleaned with trichloroethane, acetone and alcohol. This non-aqueous preparation technique was required to prevent hydration of the borosilicate glasses formed during exposure of Type B and Type C-coated SiC/SiC. Due to the experimental nature of these coatings, only one sample of each type was available for oxidation at each of the three temperatures.

## Results and Discussion

Figure 2 contains the kinetic curves for the Type U (uncoated) material. The initial weight loss is due to oxidation of the exposed carbon interface material. The subsequent weight gains are due to SiC and Nicalon fiber oxidation. X-ray maps of the interior of the exposed samples confirm that the carbon interface is completely oxidized and silica (SiO<sub>2</sub>) has formed in its place.

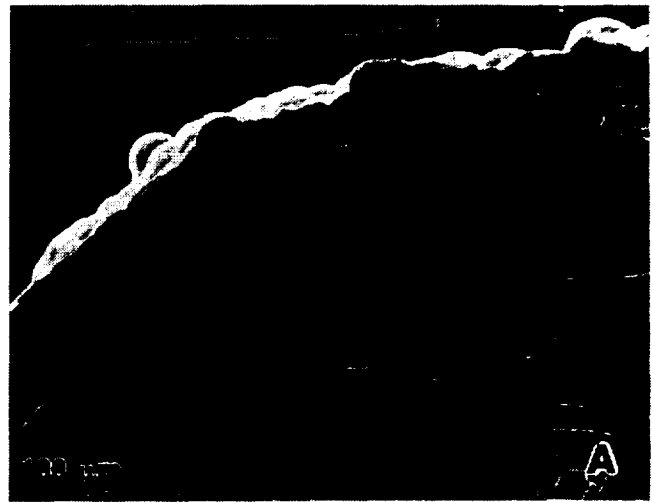


Figure 1.a. Cross section of Type A SiC/SiC (CVD SiC coating).

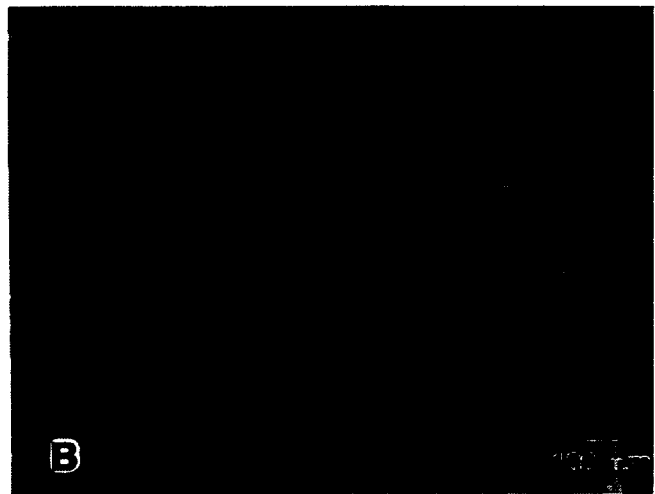


Figure 1.b. Cross section of Type B SiC/SiC (particulate-based inner sealant layer and outer CVD SiC coating).

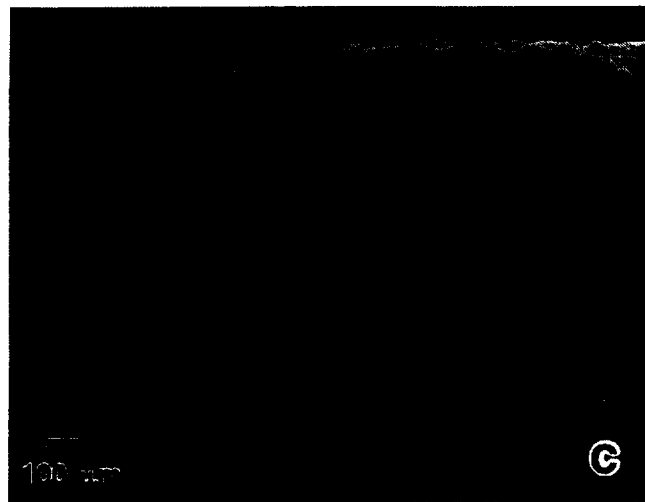


Figure 1.c. Cross section of Type C SiC/SiC (boron-rich inner layer and outer CVD SiC coating).

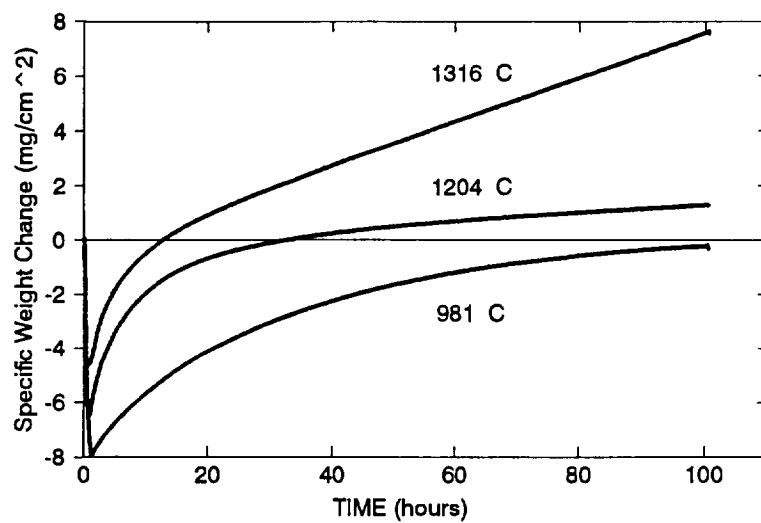


Figure 2. Oxidation kinetics of Type U (uncoated) SiC/SiC.

The Type A material exhibits parabolic oxidation kinetics at the two lower temperatures (Fig. 3). Thin silica scales were observed on the samples after oxidation. The parabolic rate constant ( $K_p$ ) measured at 1204°C was  $3.0 \times 10^{-4} \text{ mg}^2/\text{cm}^4 \text{ h}$ . By comparison, the  $K_p$  measured on a bulk monolithic CVD SiC under these same conditions in a previous study was  $1.5 \times 10^{-4} \text{ mg}^2/\text{cm}^4 \text{ h}$ . The kinetics at 1316°C deviate from parabolic. This is likely due to decomposition of the Nicalon fibers that results in the formation of a non-protective, porous oxide scale. No weight loss was observed for any of the Type A samples. X-ray maps of polished cross sections after exposure confirm that carbon remains at the matrix/fiber interface.

Figure 4 contains the kinetic curves for the Type B material. Note that the measured weight gains are an order of magnitude higher than that observed for Type A SiC/SiC. No weight loss is noted. Low parabolic kinetics are observed at 981°C. However, large weight gains are observed at the two higher temperatures. At 1204°C, one corner of the sample reacted with the sample cup. A crack in the outer SiC layer of the duplex coating evolved from this reaction site. A glass is observed in the vicinity of the crack. As discussed above, the purpose of this glass is to seal the crack and inhibit oxidation. A polished cross-section of Type B SiC/SiC after 100 h at 1204°C in dry oxygen is shown in Fig. 5. The crack in the outer CVD SiC layer of the duplex coating is denoted by Arrow 1. A small crack observed in the substrate SiC matrix is denoted by Arrow 2. X-ray maps of the area just below this crack (Fig. 6), an area where one would expect enhanced oxidation, reveal that carbon is still present at the fiber/matrix interface. The surface oxide of the 1316°C sample is quite porous, which leads to the enhanced kinetics. This porous nature could result from gas evolution from decomposition of the Nicalon fibers or volatilization of a boron-containing surface glass. SEM/EDS shows carbon to be present in the sample interior. From the kinetic curves and interior X-ray analysis, it is clear that coating Type B protects the interface from oxygen under the conditions of this study.

The Type C coating also contains boron, and borosilicate surface glass is observed after exposure at the two higher temperatures. Oxidation kinetics are enhanced (Fig. 7) because the oxide is liquid at the test temperature. A cross section of Type C coated SiC/SiC after 100 h at 1204°C in dry oxygen is shown in Figure 8. A crack in the outer SiC layer allows oxygen penetration to the boron-containing inner layer of the coating. A borosilicate glass forms and acts to seal the crack. As shown in Fig. 8, some of the glass also travels down cracks in the inner CVI SiC of the composite to the near-surface fiber bundle. Only minor oxidation of the interface is observed. X-ray dot maps of polished

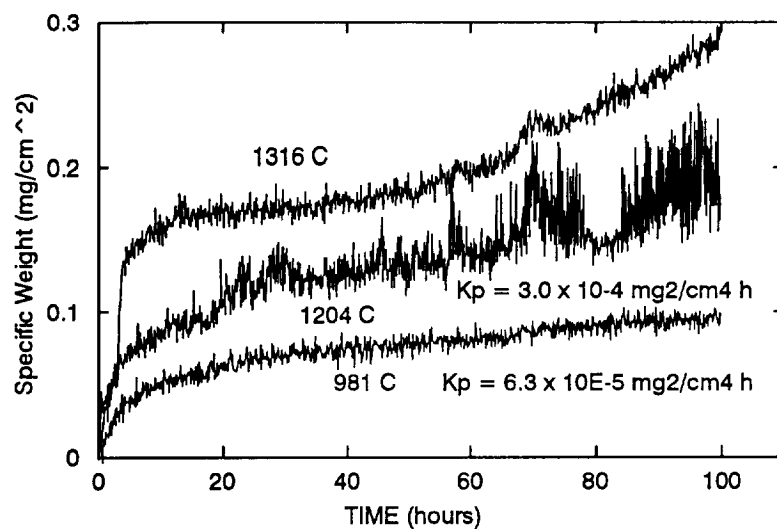


Figure 3. Oxidation kinetics of Type A SiC/SiC.

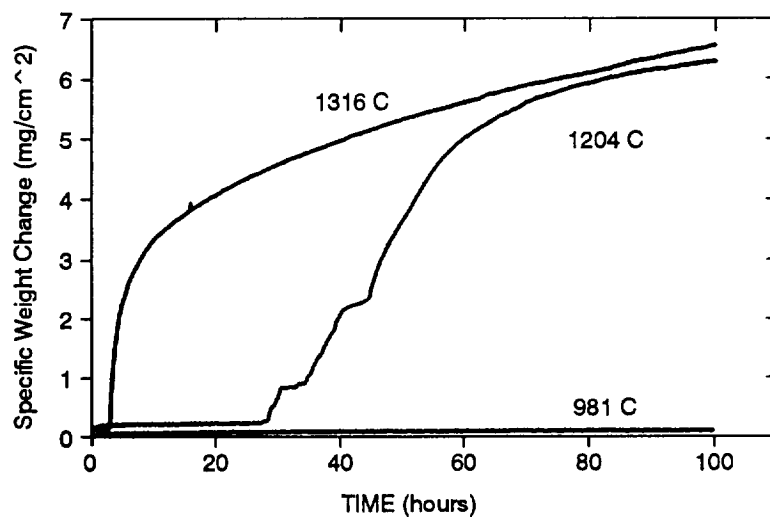


Figure 4. Oxidation kinetics of Type B-coated SiC/SiC.

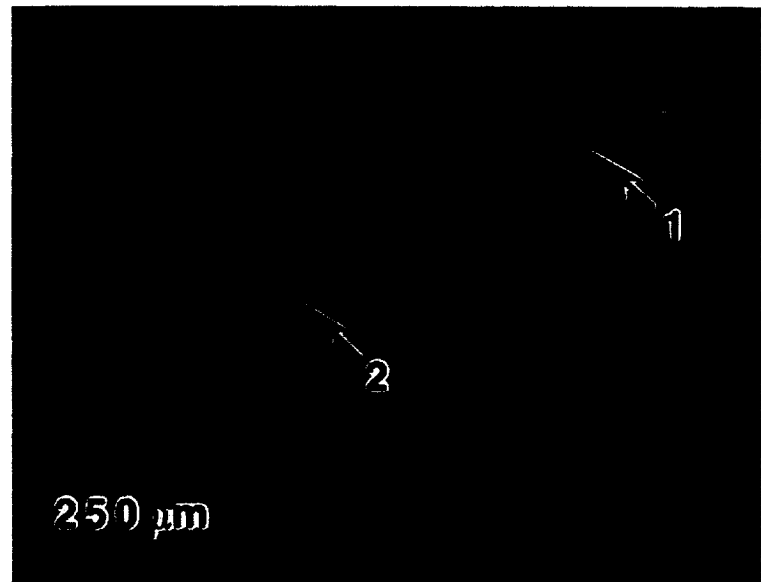


Figure 5. A cross-section of Type B SiC/SiC after 100 h at 1204°C in dry oxygen. Arrow 1 points to the crack in the outer SiC layer of the duplex coating. Arrow 2 points to the area just below a crack in the substrate analyzed for carbon using SEM/EDS.

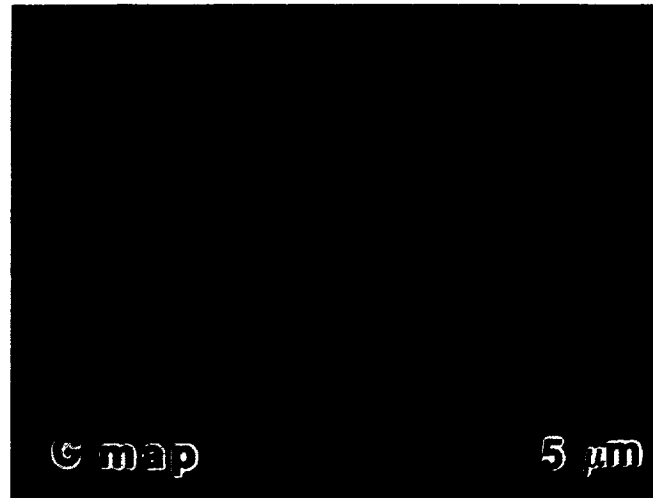


Figure 6. Carbon X-ray dot map of the area denoted by arrow 2 in Fig. 5.



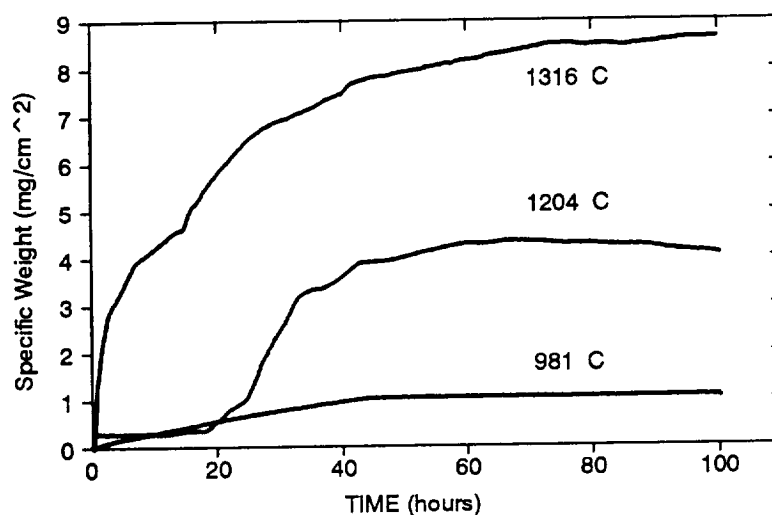


Figure 7. Oxidation kinetics of Type C-coated SiC/SiC.

cross sections at all three temperatures show carbon at the interface. As with the other two coatings, coating Type C adequately protects the interface from oxidation under the conditions of this study.

One must be aware of the possible problems associated with the surface borosilicate glass observed after exposure of Type B SiC/SiC at 1204°C and Type C SiC/SiC at 1204° and 1316°C. Surface oxidation will be enhanced because the boron-containing oxide is liquid at temperature, as compared to the solid silica formed on Type A material. Carbon oxidation will be inhibited as long as the glass is present. However, the glass may volatilize or actually be driven off of the sample by the high velocities typical of actual engine operating environments. If the glass is no longer present, oxidation of carbon at the interface will occur rapidly. Another concern is hydration of the glass that could cause its rapid depletion. Burner rig oxidation experiments are currently underway in these laboratories on Type C coated SiC/SiC. A burner rig closely models the high velocity conditions encountered in a gas turbine. Utilizing kerosene as the fuel, the oxidizing gases will include not only oxygen, but also water vapor and carbon dioxide. In 100-hour tests wherein weight gains are measured, exposed Type C SiC/SiC tensile samples retain their as-fabricated room-temperature strengths.

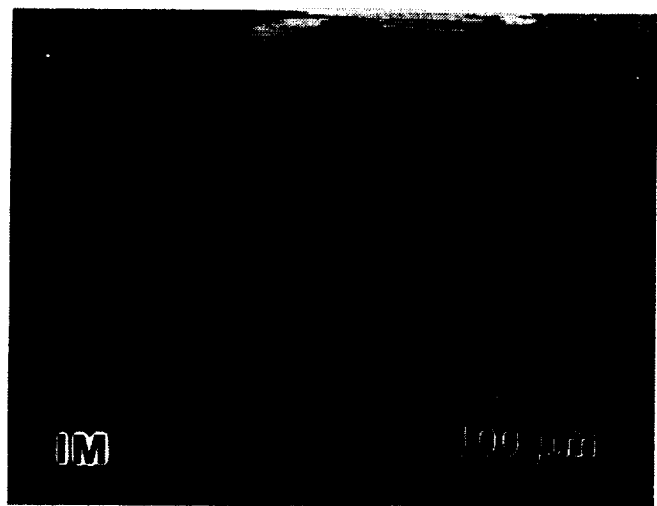


Figure 8.a. Cross-section of Type C SiC/SiC after 100 h in dry oxygen.

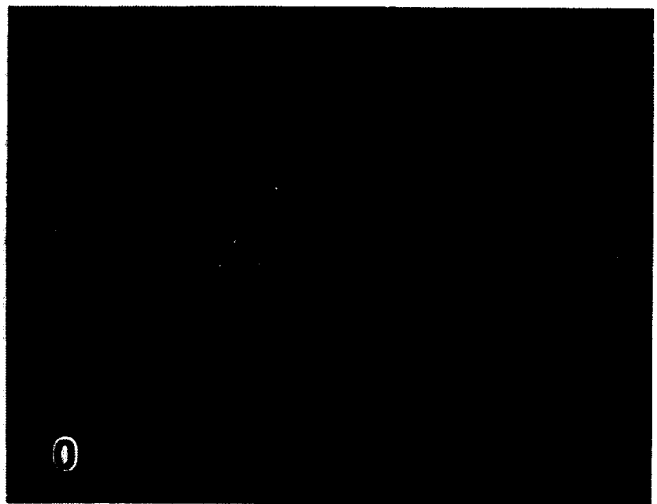


Figure 8.b. Type C SiC/SiC after 100 h in dry oxygen; Oxygen map.

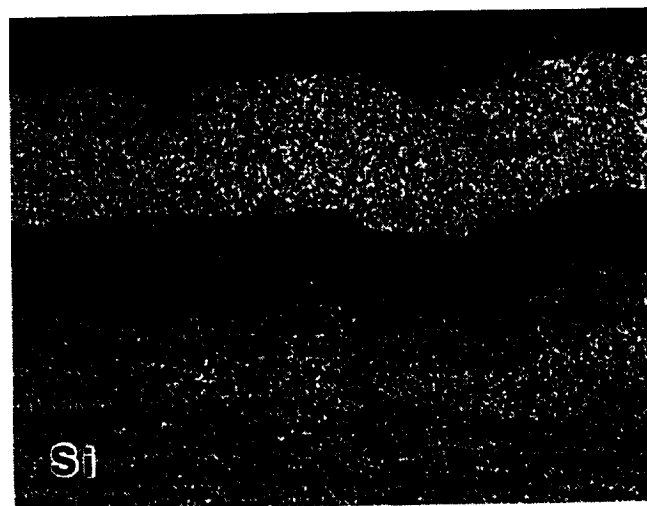


Figure 8.c. Type C SiC/SiC after 100 h in dry oxygen; Silicon map.

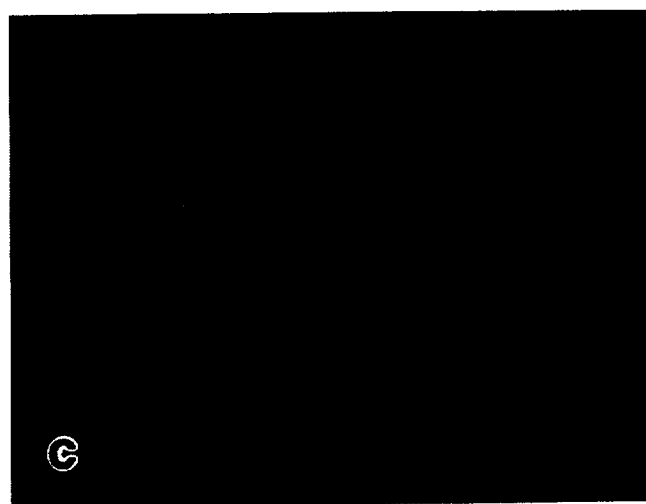


Figure 8.d. Type C SiC/SiC after 100 h in dry oxygen; Carbon map.

## SUMMARY AND CONCLUSION

A continuous silicon carbide fiber-reinforced silicon carbide matrix composite (SiC/SiC) was exposed to a dry, flowing oxygen environment at 981°, 1204° and 1316°C. The oxidation kinetics were determined via thermogravimetric analysis. Three different external coating systems were effective in protecting the carbon interface from oxidation for the 100 hours of exposure time. Coating Type A (CVD SiC) is the most promising due to low oxidation kinetics resulting from solid silica formation. Oxidation is enhanced due to the formation of borosilicate surface glass at 1204° and 1316°C in both Type B and Type C coatings. The enhanced oxygen diffusion through the glass, as compared to pure SiO<sub>2</sub>, results in accelerated oxidation kinetics. The glass seals surface cracks and inhibits oxygen penetration. In conclusion, the carbon interface in SiC/SiC is adequately protected by all three coatings under low flow conditions in dry oxygen. Hydration of the surface borosilicate glass that was formed during exposure of Type B and Type C materials can result in sealant depletion. This may limit the useful lifetime of those materials in environments where this effect occurs.

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